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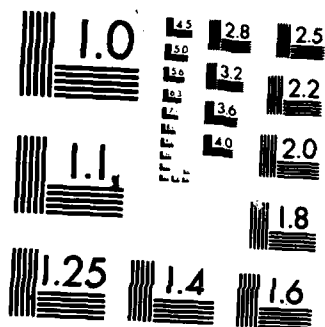
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by

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Temperature Dependent Ferroelectric Hysteresis Study
in Polyvinylidene Fluoride

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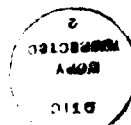
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Abstract

→ An experimental study of temperature dependent ferroelectric hysteresis phenomena of polyvinylidene fluoride is presented. The temperature dependence of the remanent polarization and coercive field was measured from saturated ferroelectric hysteresis curves with a temperature range from 60 °C to 130 °C. This data was then compared to a 2-site and 6-site ferroelectric switching model. ←



A

The large piezoelectric coefficients in polarized polyvinylidene fluoride (PVDF) have stimulated a great deal of interest in this polymer since its discovery⁽¹⁾. Experimental evidence now indicates this material is ferroelectric⁽²⁻¹¹⁾, and some features of the ferroelectric behavior have been shown to be consistent with the properties of a simple cooperative model⁽¹²⁾. This letter presents temperature dependent saturated ferroelectric hysteresis data for specially prepared low conductivity samples of PVDF. The data are fitted to results calculated for a two-site and six-site cooperative model.

Experimental

Uniaxially oriented samples of polyvinylidene fluoride, Solvay 1008⁽¹³⁾, 28 μm thick, were evacuated to 50 millitorr at 100 °C overnight. This treatment increased both the dielectric strength and the electrical resistivity of the sample. The electrical resistivity of the samples was approximately increased by a factor of five at room temperature and a factor of forty at 100 °C. Aluminum electrodes (5 cm^2) were vacuum deposited on the films and leads were attached with silver epoxy. A single sample was placed in a forced convection oil bath at elevated temperature. The electrical hysteresis (D vs. E) was measured with a Sawyer-Tower circuit⁽¹⁴⁾ which was modified as described earlier⁽⁸⁾ to compensate for conduction currents in the sample. Some decrease in the remanent polarization was observed after repeated electric field cycling at temperatures above 100 °C. Therefore, several samples were measured at each temperature with each sample cycled for about ten minutes. The measured polarization had a strong dependence upon frequency for frequencies greater than 0.5 Hz. In the frequency range of this observation, 0.01 to 0.02 Hz, the frequency dependence of the polarization was small.

Examples of saturated ferroelectric hysteresis loops observed during our measurements are shown in Figure 1. Remanent polarization (P_r) and coercive field

(Ec) were taken to be the intersections of the hysteresis loop with the E=0 and D=0 axes respectively. The hysteresis was assumed to be saturated when an increase in the maximum electric field by approximately 10% produced no detectable change in Pr or Ec.

Figure 2 shows the measured Pr and Ec values versus temperature. Measurements taken without a compensating current indicated that at the highest temperatures the conduction charge was comparable in magnitude to the induced polarization. We estimate that the error in reading Pr and Ec from the oscilloscope screen was about $\pm 3\%$ and the error in Pr due to uncertainty in current compensation may be large at the highest temperatures but is undetermined. The analytical expressions to which the data were fit were derived as follows.

Model

By minimizing the Helmholtz free energy for a cooperative dipole model it has been shown in the author's (MGB & GTD) previous work⁽¹²⁾ that

$$-2U_0 f_1 - m_e E \cos \theta_1 + kT (1 + \ln f_1) - \lambda = 0, \quad (1)$$

where $f_1 = f(\theta_1)$, represents the fraction of all dipoles of moment m_e oriented at an angle θ_1 with respect to the applied electric field, E, U_0 = energy difference between an orientation site when it is completely filled by dipoles and when it is empty, and λ = a Lagrange multiplier.

The set of equations (1) can be solved for any number of sites i and any distribution of site orientations θ_i . Here we consider only two cases - the classical two site model with $\theta_2 = \theta_1 + \pi$ and the six-site model with $\theta_i = \theta_1 + (i - 1) \pi/3$ appropriate to the nearly hexagonal packing of molecules in the β phase crystals of PVDF⁽⁷⁾. For the model, the remanent polarization is the equilibrium polarization given by solving eqs. (1) at E=0 and the coercive field is taken to be the minimum field for which solutions to eqs. (1)

cease to exist. In the following, θ_1 will be chosen as the direction of applied field ($\theta_1=0$) and for simplicity we consider a single crystal rather than an assembly of crystals of different orientations.

For the two-site model we write the polarization $P=(f_1-f_2) P_0$ where P_0 is the maximum polarization possible ($f_1=1$). Subtracting eq. (1) for f_2 from eq. (1) for f_1 gives,

$$-\frac{2 U_0}{kT} \left[\frac{P}{P_0} \right] - \frac{2 m_e E}{kT} \cos \theta_1 + \ln \left[\frac{1 + P/P_0}{1 - P/P_0} \right] = 0 \quad (2)$$

which for $E=0$ and $T_c = U_0/k$ can be expressed in the familiar form⁽¹⁵⁾,

$$P/P_0 = \tanh \left[\frac{T_c P}{T P_0} \right] \quad (3)$$

We can solve eq. (3) for T/T_c to obtain the desired remanent polarization at various temperatures. To obtain the coercive field, E_c , we let $dE/d(P/P_0)=0$, and solve for $P/P_0 = \pm \sqrt{1-T/T_c}$. This polarization is substituted into (2) to obtain

$$E_c = \frac{U_0}{m_e} \sqrt{1-T/T_c} - \frac{kT}{2m_e} \ln \left(\frac{1+\sqrt{1-T/T_c}}{1-\sqrt{1-T/T_c}} \right) \quad (4)$$

The six-site model can be treated similarly for the remanent polarization. Since $f_1 > f_2=f_3=f_4=f_5=f_6$ (at $E=0$) then $P/P_0=(f_1-f_4)$ (the other moments cancel) and $f_4=(1-f_1)/5$. Subtracting eq. (1) for f_4 from eq. (1) for f_1 and substituting P/P_0 gives

$$-\frac{2 U_0}{kT} \frac{P}{P_0} + \ln \left[\frac{1+5P/P_0}{1-P/P_0} \right] = 0. \quad (5)$$

When one examines P/P_0 as a function of U_0/kT in equation 5, one finds that the polarized state becomes unstable when $2U_0/kT = 3.8364$. Equating this condition with the Curie point, we can assign $2U_0 = 3.8364 kT_c$ and rewrite equation 5 as

$$T/T_c = 3.8364 (P/P_o) \left[\ln \left(\frac{1+5P/P_o}{1-P/P_o} \right) \right]^{-1} \quad (6)$$

There is no simple way to solve equations (1) for the coercive field in the six-site model so we use a numerical iterative process previously employed⁽¹²⁾. The numerically determined values of E_c are closely approximated by the linear expression,

$$E_c = 1.92 (k/m_e) (T_c - T). \quad (7)$$

Data Fits

Non-linear least squares fits of the P_r data to equations (3) and (5) and of the E_c data to equations (4) and (7) were performed. The P_r value obtained at the highest temperature was omitted from the fit. The values of the parameters resulting from the fits and their 95% confidence limits are shown in Table I, and graphical representations of the theoretical expressions evaluated with the use of the parameters in Table I are shown in Figures 3a and 3b, along with the data. Both the 2-site and 6-site models fit the data well, and data over a broader temperature range would be needed to distinguish between these two models.

Discussion

The value of T_c has been estimated to be in the range of 470 - 485 K from extrapolations of T_c values of VDF-TrFE copolymers to 100% VDF^(16,17). The values determined here from the E_c data seem unreasonably high and the values from the P_r data too low. One difficulty in comparing experimental data with expectations from the model is that the calculated values apply to a single crystal orientation of dipoles whereas the experimental samples have a distribution of orientations about the draw direction. The effects of this difference are that the experimentally observed coercive fields will be larger than and the observed polarizations smaller than the calculated values.

An important difference between the two models considered here is the transition is first order for the six-site model. The data force the transition for the 6 site model to occur at a temperature which has been shown to be unreasonably low⁽¹⁸⁾.

The maximum polarizations of 7.4 and 8.4 $\mu\text{C}/\text{cm}^2$ derived from the fit are somewhat lower than the value of 10 $\mu\text{C}/\text{cm}^2$ estimated from the vacuum moment of the monomer $m_v = 7 \times 10^{-30}$ cm, the enhancement due to the reaction field $m_o = m_v (\epsilon_c + 2)/3 = 11.7 \times 10^{-30}$ Cm (where ϵ_c is the crystal permittivity) and the concentration of dipoles in the crystalline phase of a 50% crystalline sample⁽¹⁹⁾. Values of m_e of 57.3 and 131 $\times 10^{-30}$ Cm obtained from the least squares fit correspond to 4.9 and 11.2 monomer units. A kink model which considers rotations about carbon-carbon bonds⁽²⁰⁾ has found the kink length to be about 4 to 5 monomer units long, and this quantity might reasonably be compared to the m_e values above.

Conclusion

Electric charge was measured as a function of applied voltage for uniaxially oriented films of polyvinylidene fluoride. Well-formed hysteresis loops were obtained from 60 °C to 130 °C and the polarization and coercive field were determined from these data. Two-site and six-site cooperative models were analyzed and the calculated remanent polarizations and coercive fields were compared to the experimental values. The data was not able to distinguished between the two models.

Acknowledgements

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Table I Parameters Determined From Least Squares Fits

Coercive Field Fit

	$\frac{m}{e}, \text{Cm}$	T_c, K
2-site Eq. (6)	$57.3 \pm 1.3 \times 10^{-30}$	692 ± 6
6-site Eq. (7)	$131 \pm 1 \times 10^{-30}$	566 ± 7

Remanant Polarization Fit

	$P_0, \mu\text{C}/\text{cm}^2$	T_c, K
2-site Eq. (3)	8.45 ± 0.11	459 ± 11
6-site Eq. (4)	7.40 ± 0.10	392 ± 11

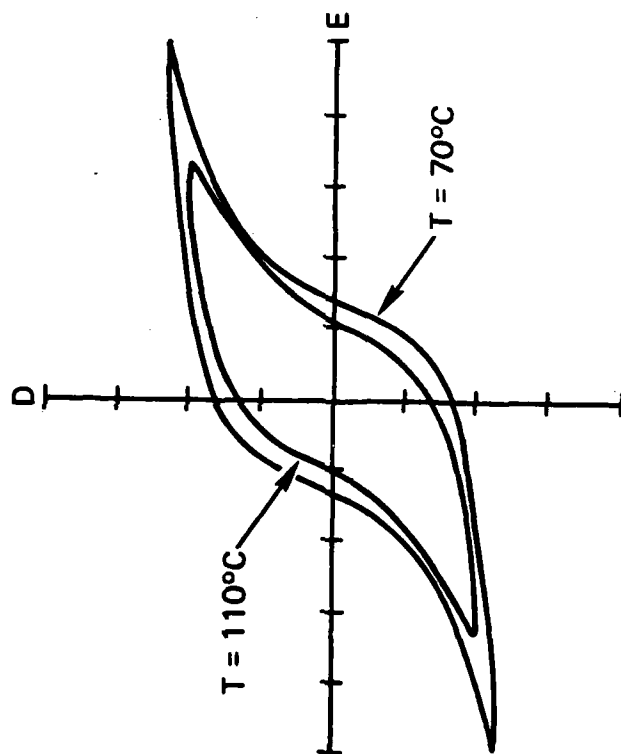
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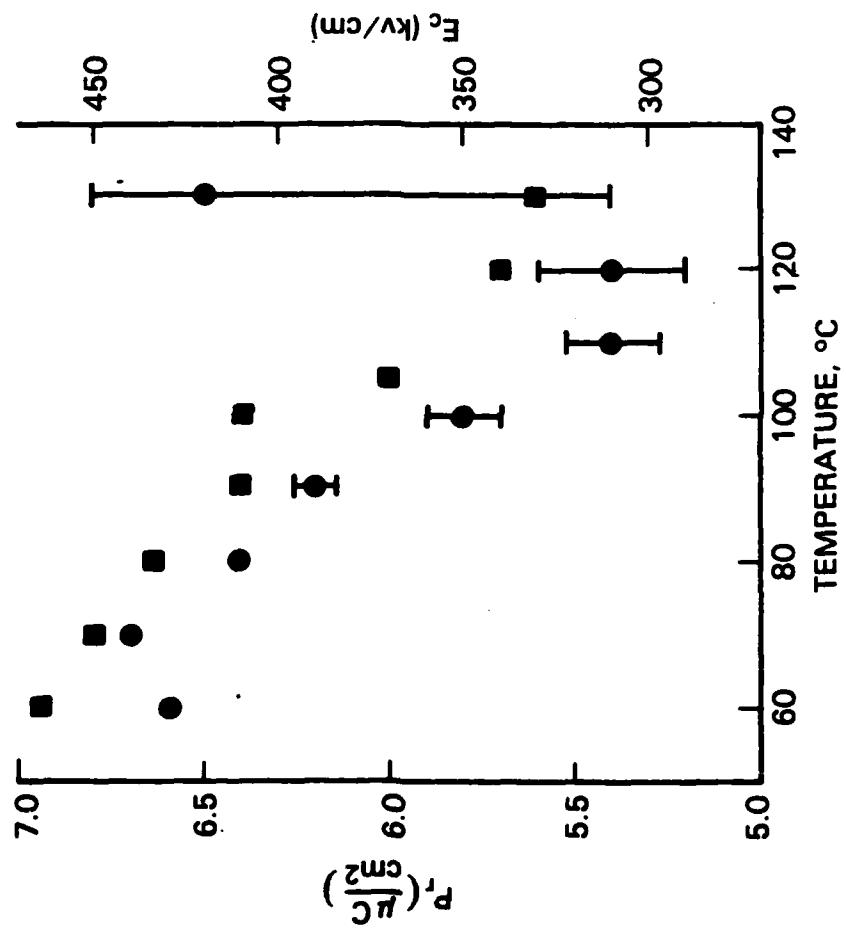
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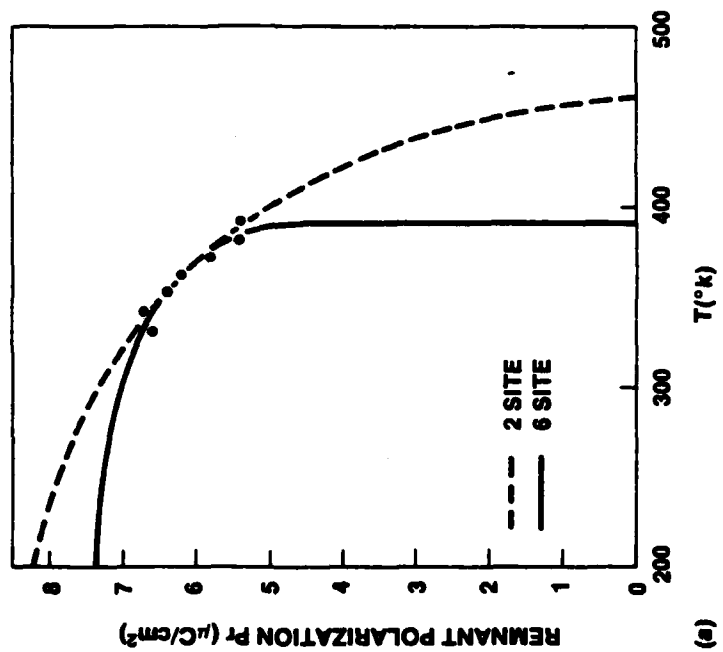
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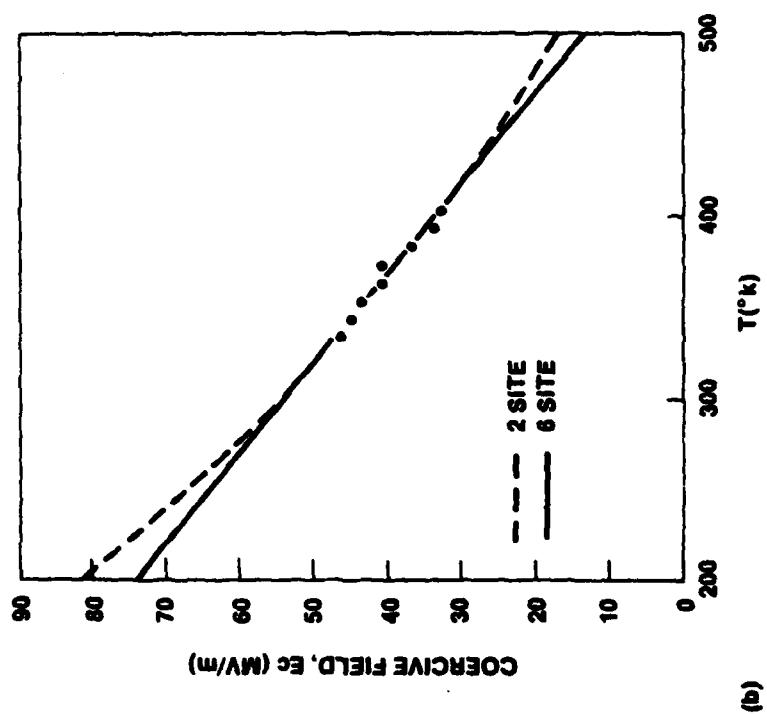
Figure Captions

1. Typical saturated ferroelectric hysteresis curves observed with compensated Sawyer-Tower circuit.
2. Remanent polarization and coercive field as measured from hysteresis curves as a function of temperature with the dots being P_r and boxes being E_c .
3. (a) Remanent polarization data and the predicted curves for the 2-site and 6-site models evaluated using the least squares P_r and T_c values of Table I. (b) Coercive field data and the predicted curves for the 2-site and 6-site models evaluated using the least squares E_c and T_c values of Table I.









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